Kinetics, Mechanism And Product Yields in the Atmospheric Oxidation of Dimethylsulfide

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LONG-TERM GOALS

Dimethylsulfide (DMS, CH_3SCH_3) produced by phytoplankton emission is thought to be the major source of the sulfate and methanesulfonate aerosol found in the marine boundary layer. An understanding of the mechanism of formation of these aerosols is critical to understanding the factors which control visibility in the marine boundary layer. The primary objective of this research effort is the determination of the detailed mechanism of, and final products yields from, the OH initiated gas phase oxidation of dimethylsulfide (DMS).

OBJECTIVES

Our objectives include a) the determination of the elementary rates for adduct formation, decomposition and reaction, b) direct confirmation of production, and quantitative product yields of potential reaction products and intermediates such sulfur dioxide (SO_2) and dimethyl sulfoxide (DMSO: $(CH_3)_2SO$), c) determination of the homogeneous and heterogeneous removal rates of the stable primary products of DMS oxidation.

APPROACH

Our gas phase studies utilize the Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence (PLP-PLIF) technique. Laser photolysis of a suitable precursor, either H_2O_2 or HNO_3, is used to generate OH. The rate of loss of OH, and the appearance of potential products such as SO_2, SO and CH_3S are monitored by a second "probe" laser using laser induced fluorescence. Kinetic information is obtained by varying the delay between the photolysis and probe lasers, mapping out a temporal profile of the species of interest.

WORK COMPLETED

Our current proposal identified discrepancies in the experimental data base on DMS chemistry and led us to conclude that there was a significant possibility that the currently recommended rate coefficient for

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the reaction of OH with DMS under atmospheric conditions is too slow. An accurate value of this rate coefficient is critical in defining the lifetime of DMS in the marine boundary layer and hence the rate at which it is oxidized to products, some of which may act as condensation nuclei. We identified the following measurement as critical. "*Definitive measurements of the forward addition rate at high pressure are critical to resolving this issue and in allowing us place definitive limits on the extent of OH regeneration at high pressure and hence on the effective rate coefficient for reaction 1 under atmospheric conditions.*" The forward addition rate refers to the rate of formation of the OHDMS and OHDMS-d_6 adducts:

$$OH + (CH_3)_2S + M \leftrightarrow (CH_3)_2SOH \qquad (1b,-1b)$$
$$OH + (CD_3)_2S + M \leftrightarrow (CD_3)_2SOH \qquad (2b,-2b)$$

In previous ONR supported work (Hynes et al., 1995) we reported values for the forward addition rate, k_{2b}, at 100 Torr over the temperature range 250-261 K using H_2O_2 as our OH precursor but we were unable to extend the measurements to lower temperatures or higher pressures. In addition we were unable to obtain data at delays shorter than 2 μsecs at 250 K. We have now revamped our optical detection system using a redesigned reaction vessel, purchased a new set of high performance narrowband dichroic filters for OH detection, and redesigned our detection filterpack. This has resulted in a dramatic improvement in our overall OH detection sensitivity. We have succeeded in obtaining data using H_2O_2 as our OH precursor at 240 K at pressures as high as 600 Torr in N_2. The data are of high quality and are consistent with our hypothesis that currently recommended rate coefficient for the reaction of OH with DMS under atmospheric conditions is too slow. To compare these results with the variation in the effective rate coefficient for reaction 2, k_{obs}, we also measured the variation in k_{obs} as a function of oxygen partial pressure at 600 Torr total pressure. One possible check on OH regeneration involves a comparison of the rate coefficients obtained for the rates of ^{16}OH and ^{18}OH with DMS. In these experiments we have to use $H_2^{18}O$ as out source of ^{18}OH via the reaction:

$$O^1D + H_2O \rightarrow 2\ OH$$

In our case we photolyze normal ozone, $^{16}O_3$, as our photolysis source because the cost of the $^{18}O_2$ required to make $^{18}O_3$ is prohibitive. Hence we make a mixture of ^{16}OH and ^{18}OH via the reaction sequence:

$$^{16}O_3 + h\nu_{266nm} \rightarrow {}^{16}O^1D + O_2$$

$$^{16}O^1D + H_2^{18}O \rightarrow {}^{18}OH + {}^{16}OH$$
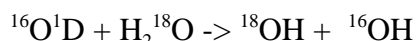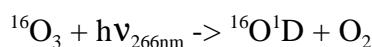
We then monitor the decay of the respective isotopomers using their OH A-X (1-0) $Q_1 1$ lines which are $6cm^{-1}$ apart.
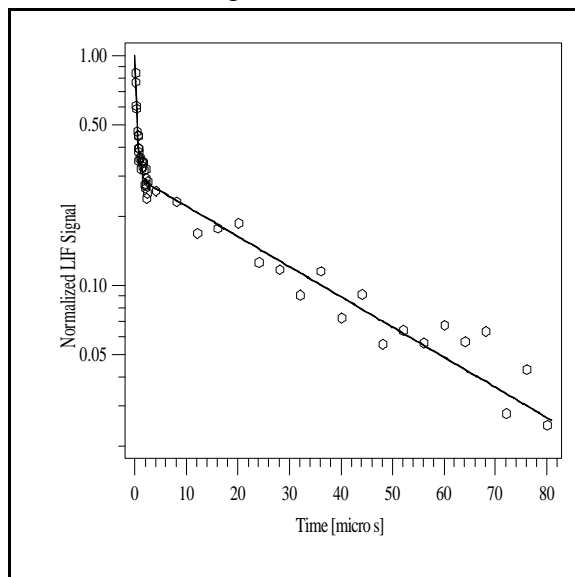
RESULTS

Figure 1 shows an example of a double exponential decay of OH in the presence DMS-d_6 in 600 Torr of N_2 at 240 K. If the OH initiated oxidation of DMS can be described by the reaction sequence

$$CD_3SCD_3 + OH \rightarrow CD_3SCD_2 + HOD \qquad (2a)$$
$$CD_3SCD_3 + OH + M \rightleftharpoons CD_3S(OH)CD_3 + M \qquad (2b)$$
$$CD_3S(OH)CD_3 + O_2 \rightarrow Products \qquad ` \qquad (3)$$
$$OH \rightarrow loss\ by\ diffusion\ or\ background\ reaction \qquad (4)$$

Under pseudo-first order conditions, i.e. [DMS-d_6] $\gg$ [OH], the OH temporal profile should be described by a double exponential expression [Hynes et al, 1995].

Fig. 1

We can determine our elementary rate coefficients by fitting our observed decays to such an equation and solving to obtain the elementary rate coefficients from each decay. The solid line in Fig 1 shows the results of such a fit and gives the elementary rates:

$$k_{2a} = 2.09 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$k_{2b} = 3.58 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$k_{-2b} = 7.6 \times 10^5 \text{ s}^{-1}$$

We can then average the results of the individual determinations which gives a values of $k_{2b} = (5.17 \pm 3.54) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} ($\pm 2\sigma$). Unfortunately, the error in the rate coefficients extracted from such decays have rather large uncertainties. This is due to the fact that both components of the double exponential have relatively fast decay components. An alternate approach plots α vs[CD$_3$SCD$_3$] (see eqn. [I], Hynes et al., 1995) and gives an averaged value of ($k_{2a} + k_{2b}$). Using this approach we obtain $k_{2b} = (4.49 \pm 2.85) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} ($\pm 2\sigma$).

These results are clearly incompatible with the 1986 values derived by Hynes et al. which obtained a value for k_{2b} of 1.3×10^{-11} cm^3 molecule^{-1} s^{-1}. To compare this value with the "limiting" value of k_{obs} we measured k_{obs} as a function of O$_2$ concentration at 240 K and a total pressure of 600 Torr. Fig. 2 shows the roll-off curve which is clearly reaching a limiting value of 2.5×10^{-11} cm^3 molecule^{-1} s^{-1}. The value of the 600 Torr rate coefficient in air is 70% faster than the projected value for 240 K given in the 1986 paper of Hynes et al., however it is significantly less than our measured value of k_{2b} although it lies within the combined error bars. We note that this discrepancy is again suggestive that OH regeneration may be causing us to underestimate k_{obs}.

To examine this possibility we have begun measurements to determine the rate coefficient for the reaction of ^{18}OH with DMS using O^{1}D + H$_2^{18}$O. This is an extremely difficult measurement at high

pressure in the presence of O_2 or N_2 since quenching of O^1D to O^3P will dominate

Fig. 2
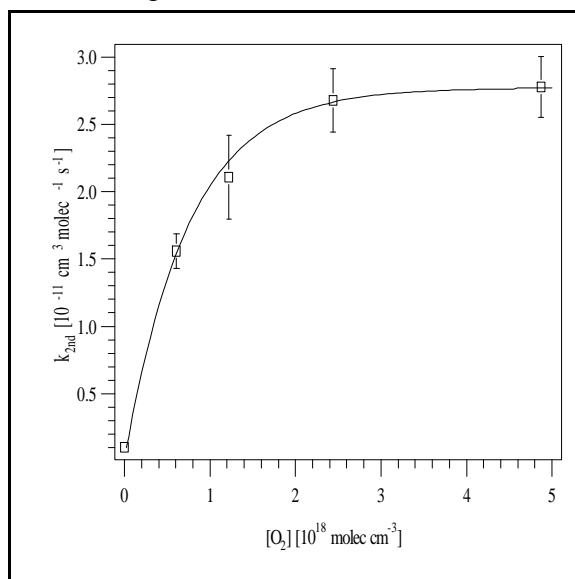
with reaction to produce OH being a minor channel. In our kinetic experiments we monitor ^{16}OH via excitation of the Q_11 line at 281.96 nm or the Q_11 line of ^{18}OH at 282.01 nm.. Lif spectra, taken with our MOPO 730, show that we can clearly distinguish between the Q_11 lines of the isotopomers and monitor them independently. In experiments in He we obtain similar rate coefficients for both ^{18}OH and ^{16}OH which are in reasonable agreement with our prior work. In the presence of O_2 the kinetic decays we obtain by monitoring ^{16}OH are biexponential and show very clear evidence of secondary chemistry which regenerates OH. However for the ^{18}OH we have obtained preliminary data which suggests that this approach may be viable. This shows that the secondary chemistry arises from reactions involving either O^3P or O_2. Since these are exclusively ^{16}O their chemistry cannot regenerate ^{18}OH. We plan to attempt an alternate approach to this reaction by using vibrationally mediated photodissociation of $H_2^{18}O$ we may give us a way to produce ^{18}OH exclusively and with no secondary chemistry.

IMPACT

This is the first determination of the OHDMS adduct formation rate at pressures which are close to those in the real atmosphere. This work shows that the rate coefficient for adduct formation derived in the 1986 study of Hynes et al. is a factor of 5 too slow. It also shows that the expression derived for k_{obs} in the 1986 paper underestimates the real rate at 240 K by almost a factor of 2 even if OH regeneration is not significant. Since all current models use the 1986 expression they will significantly underestimate the oxidation rate of DMS and its contribution to new particle formation both at high latitudes in the marine boundary layer and in the middle and upper troposphere.

TRANSITIONS

The potential implications of this work for particle formation in the marine boundary layer will require a completion of the laboratory work and modeling studies.

RELATED PROJECTS

In our NSF sponsored work on HO_x cycling we have shown that the quantum yield for O^1D formation from ozone photolysis has a significant long wavelength component, part of which is spin forbidden. Our work shows that spin forbidden photolysis of ozone in the Huggins bands occurs out to at least 375 nm. This implies that current models underestimate OH concentrations, particularly at low temperatures and high zenith angles. Since OH is a primary oxidant for both DMS and SO_2 these results will feedback into models of marine boundary layer chemistry and imply higher oxidation rates of both DMS and SO_2 In related ONR sponsored work we are attempting to develop novel laser based instrumentation to allow near real-time sodium measurements on individual, size-segregated marine aerosols.

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